DEPTH DISTRIBUTION OF CHEMICAL PHASE CONCENTRATION DETERMINED BY GRAZING INCIDENCE X-RAY DIFFRACTION

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1. Introduction

Grazing incidence geometry is widely used in X-ray diffraction analysis of thin films. Penetration depth of radiation can be easily changed by an appropriate selection of the angle of incidence α that enables obtaining information from different depths of the sample. This depth can be decreased up to a nanometer scale by approaching the critical angle α_c for total external reflection. This method therefore provides an efficient tool for the analysis of depth distribution of various structural properties, such as the crystallite size, the amorphous fraction, stress or the concentration of chemical phase. However, absorption of the radiation can be characterized by an average attenuation coefficient μ a special care has to be paid to the last property. Variation of chemical phase concentration with depth usually results in depth dependence on the attenuation coefficient. In this contribution a method for determination of depth distribution of a chemical phase is outlined. The method correctly takes into account the depth variation of the attenuation coefficient. The method is tested on thin oxidized Ir layers. The aim of this paper is a comparison two simple model cases with the experimental results.

2. Theoretical background

The intensity of X-rays penetrating the homogeneous sample in the vicinity of critical angle is [1]

$$I_{\mathrm{hom}} = I_0 \exp(-2KBx) \tag{1}$$

where B is defined as

$$B = \sqrt{\frac{1}{2}\left[\sqrt{\left(\alpha^2 - 2\delta\right)^2 + 4\beta^2} - \left(\alpha^2 - 2\delta\right)\right]} \tag{2}$$

$$\delta = \rho_e \frac{\lambda^2 r_e}{2\pi} \qquad\qquad \beta = \frac{\lambda}{4\pi}\mu \tag{3}$$

where I_0 is the intensity of the incident beam, x is the depth variable, $K=2\pi/\lambda$ is the magnitude of the wave vector, ρ_e, r_e, λ and μ are the electron density, the classical radius of the electron,

the wavelength and the attenuation coefficient, respectively. When the composition of the layer changes with depth, the parameters, ρ_e, μ, δ, β, and B become a function of x and the intensity at the depth x is given as

$$I_{in\hom}(x,\alpha) = I_0 \exp\left(-2K\int_0^x B(t)dt \right) \tag{4}$$

Let us suppose that the sample consists of several chemical phases with different values of ρ_e^j, μ_j and the weight fraction of the j–th phase varies with depth as $w_j(x)$. If the thickness T of the analyzed layer is in the range of nanometers, one can neglect the absorption of the intensity of the diffracted beam and the total amount $TA_j(\alpha)$ of the j–th phase detected by measuring at the angle α will be proportional to the integral

$$TA_j(\alpha) = SC\int_0^T w_j(x)\exp\left(-2K\int_0^x B(t)dt \right) \tag{5}$$

where the intensity of the incident beam I_0 has been included in the scaling factor SC. It should be pointed out that the weight fraction $w_j(x)$ of the j–th phase appears also in $B(x)$ through the weighted values of the parameters $\delta(x)$ and $\beta(x)$ varies according to the composition of the layer at the depth x.
When the layer contains only two different crystalline phases with the weight fractions $w_1(x)$ and $w_2(x)$, their total weight fractions $W_1(\alpha)$ and $W_2(\alpha)$ will be given as

$$W_1(\alpha) = \frac{TA_1(\alpha)}{TA_1(\alpha) + TA_2(\alpha)} \qquad W_2(\alpha) = \frac{TA_2(\alpha)}{TA_1(\alpha) + TA_2(\alpha)} \tag{6}$$

The values $W_1(\alpha)$ and $W_2(\alpha)$ could be compared with experimental results at various angles α. The profiles $w_1(x)$ and $w_2(x)$ can be determined by numerical procedure using appropriate model. In the case of $w_1(x) + w_2(x) = 1$, the denominator in Eq. (6) reduces to the integral of the exponential term in Eq. (4).

3. Experimental

In order to verify the capability of our approach very thin iridium layers deposited on sapphire/GaN/AlGaN system and subsequently annealed in oxidizing atmosphere at 500° C were analyzed by X-ray diffraction. The thickness of the samples was 7nm confirmed by X-ray reflectivity measurement. The preparation and the processing of the samples are described elsewhere [2]. XRD analysis was carried out using Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW (40 kV/300 mA). All measurements were performed in parallel beam geometry with parabolic Goebel mirror in the primary beam. The diffraction patterns were recorded in grazing incidence set-up with angle of incidence α = 0.3°, 0.4°, 0.5°, 0.6° and 1.5° in the angular range 24 – 93° with the step of 0.05°.

4. Results and discussion

Two crystalline phases – Ir (PDF No. 03-65-1686) and IrO_2 (PDF No. 00-15-0870) were identified. Diffraction patterns measured at $\alpha = 0.3°$ and $1.5°$ are shown in Fig. 1. It could be observed that the Ir maxima nearly disappear in the pattern measured at $\alpha = 0.3°$, which indicates that the crystalline IrO_2 phase is concentrated at the sample surface while the pure Ir is detected only in deeper regions of the layer.

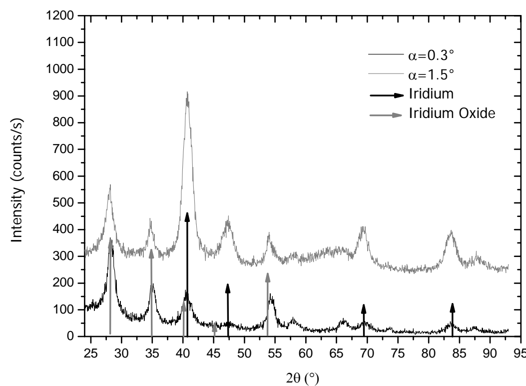

Fig. 1: Diffraction patterns of the Ir/IrO₂ sample measured at α = 0.3° and 1.5°. The diffraction maxima are marked by arrows. The upper curve is shifted for the sake of clarity.

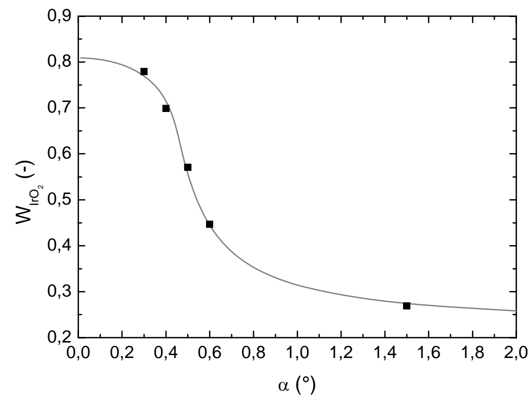

Fig. 2: Weight portion W_{IrO2} of crystalline IrO_2 phase as a function of incidence angle α. Black squares – experimental data, grey line – theoretical data calculated for the model with amorphous interlayer.

Quantitative analysis of the measurements was performed by software TOPAS 3.0. The results are shown in Fig. 2, where black squares indicate the weight portion W_{IrO2} of crystalline IrO_2 phase for various incidence angles α. The weight portion W_{Ir} of pure Ir is $W_{Ir}=1-W_{IrO2}$ according to Eq. (6). In order to explain the obtained results, two model structures of the oxidized Ir layer were examined. First one contains two crystalline phases IrO_2 and Ir with abrupt interface (Fig. 3). Free parameter is the position of the interface t_1. In the second model is an amorphous IrO_2 layer between the crystalline phases (Fig. 4). The model has two free parameters t_1 and t_2.

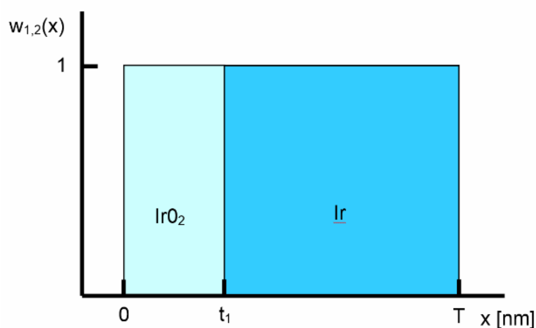

Fig. 3: Schematic drawing of the weight portions $W_{IrO2}(x)$ and $W_{Ir}(x)$ as a function of depth x for model with abrupt interface.

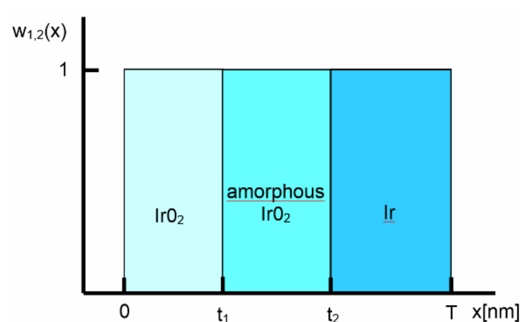

Fig. 4: Schematic drawing of the weight portions $W_{IrO2}(x)$ and $W_{Ir}(x)$ as a function of depth x for model with amorphous IrO_2 interlayer.

Detailed calculation [3] shows that first model is not able to explain the large difference between the values of W_{IrO2} – 0.78 and 0.27 measured at $\alpha = 0.3°$ and 1.5°, respectively (Fig. 2). Insertion of an amorphous IrO_2 interlayer (second model) decreases the amount of the Ir phase detected at $\alpha = 0.3°$ and increases the corresponding value of W_{IrO2}. The second model was therefore accepted as more appropriate. The parameters t_1 and t_2 were optimized by least square method. The best fit was achieved for the values $t_1=1.05nm$ and $t_2=3.22nm$. The resulting dependence $W_{IrO2}(\alpha)$ is shown in Fig. 2 (grey curve).

5. Conclusion

A method for determination of the depth distribution of chemical phase on very thin layers was proposed. The method correct describes variation of the attenuation coefficient with depth. Thin oxidized Ir layers were measured by grazing incidence X-ray diffraction at incidence angles close to the critical angle for total external reflection. Two model structures were examined and the calculated results were compared with the observed data. It was concluded that the model with amorphous interlayer is more accurate for the explanation of the experimental results.

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